

## **COUPON FOR MEASURING CORROSION RATES AND SYSTEM**

### Brief Description of the Invention

5           This invention relates generally to a coupon for measuring corrosion rates in hostile environments, to a corrosion rate measuring system employing a probe for placing the coupon in the hostile environment, and to a system for monitoring the corrosion of said coupon when it is placed in the hostile environment.

### 10   Background of the Invention

          Various attempts have been made to measure in real-time the corrosion rates of metals exposed to extremely high temperatures in hostile environments, such as those present in a coal-fired boiler. Specifically, the inner wall surfaces of a typical steam boiler are lined with tubes that carry water that, by virtue of the heat released within  
15   the boiler from the burning of a suitable fuel, is converted into steam. The metals from which boiler tubes are made are subject to corrosion in this environment and, over a period of time, these tubes can fail from surface corrosion. While temperatures within the boiler can exceed 3000°F, the surfaces of these tubes are typically at about 800°F.

20           In the past, devices have been developed that can be inserted through the boiler wall so as to expose a metal coupon to this "fireside" environment. Passive and active systems have been developed and some are commercially available. Passive systems typically expose a sample of boiler tube material to the fireside environment, while the sample is cooled and maintained at a temperature (around 800°F) representative of the  
25   tube metal surface temperature. After a predetermined time, the probe and coupon are removed and the coupon is retrieved and analyzed to determine the rate of corrosion.

In some passive systems, the coupons are prepared so that part of the surface exposed to fireside conditions is coated with a metal that is essentially inert to corrosion, while the other part of the coupon is directly exposed to the fireside environment. These types of coupons work well and have been used to determine corrosion rates. While this method will allow for the determination of a corrosion rate, it only provides this rate after being exposed for some period of time and can provide no immediate warning of failure due to a change in operating conditions or fuel.

Active systems that measure corrosion rates have been developed as well, and are commercially available. While these systems employ different methods to measure real-time rates of corrosion, all such measurements must rely on the loss of material to provide such measurements. One common approach is to measure the change in electrical resistance of a sample while it corrodes. Increasing resistance correlates to loss of material and with proper correction for those parameters that can affect the proper measurement of resistance (temperature, in particular) a corrosion rate can be determined from the accurate measurement of the change in resistance of a coupon compared to some standard. Unfortunately, these systems are typically not suitable for use in such a hostile, hot environment as that found within a boiler where it is difficult to maintain a corrosion coupon at a uniform temperature while making a measurement of the resistance of the coupon. In addition, because a macroscopic coupon will increase in resistance (corrode) at a very slow rate, very small changes in resistance must be measured in order to determine a corrosion rate. This is a considerable technical challenge, given the fireside environment.

One such active system uses an electrically isolated thin steel coupon (~0.25 mm thick) positioned in the end of an air-cooled probe. A thermocouple is attached to an indentation in the rear side of this coupon for monitoring and controlling temperature. In the fireside environment, the coupon is maintained at 800°F. To measure the resistance of the coupon, a large current (10A) is periodically passed through the coupon and an external standard resistance. While the current is maintained (for about 1 second), the voltage drop across the coupon and the external standard resistor is measured and recorded. Large currents are required because, although the coupon is small (about 50 mm across), its electrical resistance is low. Changes in the resistance of the coupon over time, when compared to the external standard resistor, are used to infer the corrosion rate.

This device suffers from a number of conceptual as well as practical difficulties. Corrosion rate is derived from the rate of loss of a section of the sensor coupon as inferred from changes in its electrical resistance. This approach assumes that the sensor coupon is thinned uniformly along its entire length, which implies that the temperature of the sensor coupon is uniform throughout and/or is accurately known. It also limits the technique to measuring corrosion rates where the mode of attack is uniform; pitting attack cannot be readily measured. A major practical problem is that, because of the high, variable heat fluxes typical of fireside conditions, it is very difficult to control the temperature of the coupon surface to a preset value.

10 The resistance of the coupon is low, whereby changes in resistance due to corrosion are small, making them difficult to measure. Even slight temperature variations result in significant changes in resistance compared to the changes due to corrosion, thus making the precise measurement of the resistance of the coupon difficult, if not impossible. The fact that the variations are dynamic rather than static represents

15 another considerable obstacle to the success of this approach. The large currents that are employed tend to heat the standard or reference resistor as well as the coupon, and thereby add uncertainty to the measurement of resistance. The fact that the coupon must be electrically isolated from the rest of the probe increases the complexity of the device. Because the change in resistance is small, measurements are not only affected

20 by temperature variations, but they are also affected by electrical transients.

### Summary of the Invention

The present invention provides a coupon which employs two or more thin-film, high-resistance metal elements carried on a substrate with one or more elements exposed to the corrosive environment while at least one element is protected from the corrosive effects of the hostile environment to provide a reference. Being mounted in close physical proximity on the same substrate, the elements are subjected to essentially the same corrosive environment, so that the effect of varying temperature is experienced by all of the elements. The advantage of high resistance is that only a

25 small current is required to produce a large voltage drop for the measurement of resistance. Corrosion of the thin film corrosion element yields a significant change in resistance, providing the capability of quickly measuring dynamically varying rates of corrosion.

30

### Brief Description of the Drawings

The foregoing and other objects of the invention will be more clearly understood from the following description when read in conjunction with the accompanying drawings in which:

5           Figure 1 is a top plan view of a coupon in accordance with the present invention, showing the corroding thin film resistance element.

          Figure 2 is a bottom plan view of the coupon of Figure 1 showing the thin film resistance reference element.

          Figure 3 is a sectional view taken along the line 3-3 of Figure 1.

10          Figure 4 is a top plan view of a coupon in accordance with another embodiment of the invention.

          Figure 5 is a sectional view along the line 5-5 of Figure 4.

          Figure 6 is a top plan view of a coupon in accordance with still another embodiment of the present invention.

15          Figure 7 is a top plan view of a coupon in accordance with a further embodiment of the present invention.

          Figure 8 is a sectional view showing a coupon mounted on a corrosion probe.

          Figure 9 is a sectional view showing a coupon mounted on a hollow bolt.

20          Figure 10 is a circuit diagram of a circuit for measuring the change in resistance due to corrosion.

          Figure 11 is a curve showing the change in resistance due to corrosion, illustrating two corrosion rates.

### Description of the Preferred Embodiment

25          Thin film corrosion elements of constant cross-section are deposited on a substrate that is electrically non-conductive or is treated to have an electrically non-conductive surface film. Small rates of corrosion of the film exposed to the hostile environment will yield a large change in its resistance.

30          The thin film corrosion elements are fabricated in one of two ways, either of which will withstand the fireside environment. In either approach, thin films of the metal of interest (for instance, iron) are sputtered or evaporated onto electrically insulating substrates. In one embodiment, two patterns are applied or deposited onto a substrate. One pattern is covered by a film of inert material, whereby it is protected

from the corrosive environment, while the other thin film pattern is exposed to the corrosive environment. The two thin patterns are positioned so that they will be subjected to substantially the same temperature environment.

In another embodiment, the patterns are deposited on opposite sides of a thin substrate, whereby only one pattern is exposed to the hostile environment. The side of the coupon not exposed to the hostile environment may or may not need to be protected by a protective layer. In another embodiment, both patterns are on the same side of the substrate and overlying one another, with one pattern protected by a corrosion-resistant layer and insulated from the top exposed pattern.

Referring now to Figures 1-3, a coupon which includes elongated thin metal conductors 11 and 12 on opposite surfaces of a disc-shaped substrate 13 is shown. The substrate may comprise a thin wafer of beryllium oxide ceramic (beryllia). While any suitable ceramic can be adapted, it appears that beryllia offers the best properties because it is an excellent electrical insulator, is easily formed into thin sheets, is chemically inert in a fireside environment, has a heat conductivity near that of steel, and has a coefficient of thermal expansion which is high enough to preclude the spalling or peeling off of films sputtered onto its surface.

Another suitable substrate is the metal alloy FeCrAlY. This alloy has the desired property that when it is heated to 2012°F (1100°C) in air and maintained at that temperature for a period of time, a very adherent, electrically-insulating, hard, thin film of alpha-alumina grows on its surface. Other substrates, such as glass, can be used for lower temperature applications.

The thin metal conductive elements can be formed employing deposition techniques known in the semiconductor processing art. Thin film elements having substantially uniform cross-sectional areas can be formed by masking the surface of the substrate 13 by photolithographic methods, forming openings in the mask conforming to the desired configuration of the resistive elements, and then depositing by sputtering or other deposition technique a thin film of metal onto the surface of the mask. The metal adheres to the substrate in the windows or openings. When metal of desired thickness has been deposited, the deposition process is terminated, and the mask is removed by dissolving or etching, leaving the conductive pattern.

In the example of Figure 1, thin film spiral metal conductors 11 and 12 are formed. The connection to the center of the spiral is made by masking and depositing

metal to form a radial conductive lead 14. This is followed by masking and depositing a suitable oxide film 16 over the conductor to protect the conductive lead 14 from the hostile environment, and electrically insulate the lead from the overlying spiral conductor to which it is connected. Finally, by masking and depositing metal, the spiral is formed with voltage and current connections 17, 18 and 19, 20, respectively. A similar process is carried out to form spiral conductor 12 on the underside of the substrate directly opposite the upper spiral. The spiral includes voltage and current connectors 22, 23 and 24, 25, respectively. Since the substrate is thermally thin, the two resistive elements 11 and 12 are exposed to substantially the same thermal environment. The conductive film on the lower surface is preferably overcoated with a protective sputtered-on oxide layer 27 to prevent corrosion.

The details of which metal to use for the thin film sensor are thought to be readily resolvable, even though it is unlikely that deposition techniques can produce the exact alloy composition (or microstructure) used for the actual components for which the corrosion rate data are desired. There is, however, sufficient understanding of the corrosion behavior of various alloy systems to allow correlation to be made between the corrosion rate of, for instance, pure iron (which could be deposited on a probe) and carbon steels that are commonly used for heat transfer tubing which is subjected to the hostile environment. Electrical connection can be made to the terminals 17, 18 and 19, 20 at the end of the spiral 11 through the substrate by providing holes in the substrate into which conductive material is deposited during the deposition of the thin film conductor. Electrical connections can be directly made to the terminals 22, 23 and 24, 25 on the spiral 12 formed on the other surface of the wafer.

In a more complex embodiment, Figures 4 and 5, the two conductive elements 31 and 32, are on the same side of an appropriate substrate material 33. They are separated by a protective oxide layer 34 that keeps the underside element 32 from experiencing corrosion. The element is subjected to exactly the same thermal environment as the upper corroding element 31. As in Figure 1, masking is used to create a pathway underneath each spiral. The essential technology is that of multilayer deposition by sputtering through multiple masks. The spiral 32 is formed on the upper surface of the substrate 33, as in Figure 1. The protective oxide layer 34 is then formed. The upper element 31 is formed after rotating the substrate by 90° to allow

for proper placement of the connection pads 36, 37 and 38, 39 for current and voltage measurement. The lower, noncorroding spiral is overcoated with the protective sputtered-on oxide layer 34. The idea is that the non-corroding layer is placed directly underneath the reacting layer on the same side of the substrate as the corroding layer.

- 5 Thus, the substrate need not be thin to maintain substantially equal temperatures on the two sides, because both resistive elements will experience the same thermal environment.

Figure 6 illustrates another configuration for a single-sided corroding and non-corroding coupon. The layouts do not explicitly require the layers to be stacked upon  
10 one another, rather the concept is that they are so close throughout their paths that they experience substantially the same thermal environment.

The coupon includes a substrate 41 on which are formed metal elements 42 and 43. The element 43 is protected by an oxide film 44. The ends of the elements include voltage and current connection pads 46. Figure 7 shows an embodiment  
15 including two corroding elements 42a and 42b laid down in connection with one protected element 43, thereby providing two real-time measurements of corrosion rate, while being referred to a single non-corroding protective metal layer. In all embodiments, connections to the various metal layers or elements are provided by depositing metal conductive material into holes formed in the substrate or by leads  
20 extending through the holes. If the substrate is a metal substrate which has been treated to form protective oxide film, holes are formed before oxidation so that an insulating oxide covers the walls of the holes. Metal leads can extend through the holes without shorting to the metal substrate. It should be apparent that other configurations for the thin film elements may be employed. The elements should  
25 provide a continuous high resistance path in which there is a substantial change in resistance as the element corrodes.

Referring to Figure 8, a coupon 51, formed in accordance with one of the embodiments discussed above, is secured to the end of the hollow probe 52 by means of a ring 53 which is threaded onto the end 54 of the hollow probe. A concentric tube  
30 56 is suitably mounted within the probe 52, and provides for directing the flow of cooling air 57 through the tube 56 to the underside 57 of the coupon. The flow of air is controlled to maintain the coupon at substantially the same temperature as the metal

whose corrosion is to be measured. Leads 59 are shown connected to the metal films of the coupon.

In another embodiment, Figure 9, a coupon 60 can be mounted at the end of a bolt 61 by a ring 62 threaded onto the end of the bolt. The bolt can be directly threaded by threads 63 into the wall of the boiler, whereby it is maintained at substantially the same temperature as the boiler tubes. There would be no necessity for cooling.

Figure 10 is a diagram of a circuit suitable for measuring the change in resistance of the corrosion element.  $R_C$  represents the resistance of the corroding element while  $R_R$  represents the resistance of the reference elements. A current  $I$  is caused to flow through the two elements. The voltage  $V_C$  and  $V_R$  across the two elements is applied to a circuit 71 configured to receive the current  $I$  and the voltages  $V_C$  and  $V_R$  and calculate the change in resistance  $\Delta R$  due to corrosion, as follows:

$$\Delta R = R_C - R_R = \frac{V_C}{I} - \frac{V_R}{I}.$$

It is apparent that other means of measuring the change in resistance using alternating or dc current are available. For example, measuring the voltage drop across the resistive elements with a volt meter or lock-in amplifier.

Figure 11 schematically illustrates the change in resistance with corrosion. Curve  $A$  shows a constant corrosion rate and curve  $B$  a corrosion rate which is increasing rapidly, signaling a potentially dangerous condition. The actual amount of corrosion can be easily calculated knowing the composition of the thin film material and the boiler tube material.

As described above, the material selected for the corrosion element should preferably be one that corrodes at substantially the same rate as the tubing or other component which is being monitored or in the alternative one for which a relationship can be calculated. The circuit can be calibrated to provide an indication of the amount of corrosion.

The corrosion elements can be made very thin and long to provide a high resistance whereby corrosion will have a large effect upon the resistance. This, coupled with the fact that the reference and corrosion elements are in close proximity,



whereby they are subjected to the same temperature, provides a highly sensitive corrosion measuring coupon and system.

The foregoing descriptions of specific embodiments of the present invention are presented for the purposes of illustration and description. They are not intended to  
5 be exhaustive or to limit the invention to the precise forms disclosed; obviously many modifications and variations are possible in view of the above teachings. The embodiments were chosen and described in order to best explain the principles of the invention and its practical applications, to thereby enable others skilled in the art to best utilize the invention and various embodiments with various modifications as are  
10 suited to the particular use contemplated. It is intended that the scope of the invention be defined by the following claims and their equivalents.

11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102  
103  
104  
105  
106  
107  
108  
109  
110  
111  
112  
113  
114  
115  
116  
117  
118  
119  
120  
121  
122  
123  
124  
125  
126  
127  
128  
129  
130  
131  
132  
133  
134  
135  
136  
137  
138  
139  
140  
141  
142  
143  
144  
145  
146  
147  
148  
149  
150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341  
342  
343  
344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370  
371  
372  
373  
374  
375  
376  
377  
378  
379  
380  
381  
382  
383  
384  
385  
386  
387  
388  
389  
390  
391  
392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488  
489  
490  
491  
492  
493  
494  
495  
496  
497  
498  
499  
500  
501  
502  
503  
504  
505  
506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547  
548  
549  
550  
551  
552  
553  
554  
555  
556  
557  
558  
559  
560  
561  
562  
563  
564  
565  
566  
567  
568  
569  
570  
571  
572  
573  
574  
575  
576  
577  
578  
579  
580  
581  
582  
583  
584  
585  
586  
587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609  
610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677  
678  
679  
680  
681  
682  
683  
684  
685  
686  
687  
688  
689  
690  
691  
692  
693  
694  
695  
696  
697  
698  
699  
700  
701  
702  
703  
704  
705  
706  
707  
708  
709  
710  
711  
712  
713  
714  
715  
716  
717  
718  
719  
720  
721  
722  
723  
724  
725  
726  
727  
728  
729  
730  
731  
732  
733  
734  
735  
736  
737  
738  
739  
740  
741  
742  
743  
744  
745  
746  
747  
748  
749  
750  
751  
752  
753  
754  
755  
756  
757  
758  
759  
760  
761  
762  
763  
764  
765  
766  
767  
768  
769  
770  
771  
772  
773  
774  
775  
776  
777  
778  
779  
780  
781  
782  
783  
784  
785  
786  
787  
788  
789  
790  
791  
792  
793  
794  
795  
796  
797  
798  
799  
800  
801  
802  
803  
804  
805  
806  
807  
808  
809  
810  
811  
812  
813  
814  
815  
816  
817  
818  
819  
820  
821  
822  
823  
824  
825  
826  
827  
828  
829  
830  
831  
832  
833  
834  
835  
836  
837  
838  
839  
840  
841  
842  
843  
844  
845  
846  
847  
848  
849  
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880  
881  
882  
883  
884  
885  
886  
887  
888  
889  
890  
891  
892  
893  
894  
895  
896  
897  
898  
899  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
916  
917  
918  
919  
920  
921  
922  
923  
924  
925  
926  
927  
928  
929  
930  
931  
932  
933  
934  
935  
936  
937  
938  
939  
940  
941  
942  
943  
944  
945  
946  
947  
948  
949  
950  
951  
952  
953  
954  
955  
956  
957  
958  
959  
960  
961  
962  
963  
964  
965  
966  
967  
968  
969  
970  
971  
972  
973  
974  
975  
976  
977  
978  
979  
980  
981  
982  
983  
984  
985  
986  
987  
988  
989  
990  
991  
992  
993  
994  
995  
996  
997  
998  
999  
1000  
1001  
1002  
1003  
1004  
1005  
1006  
1007  
1008  
1009  
1010  
1011  
1012  
1013  
1014  
1015  
1016  
1017  
1018  
1019  
1020  
1021  
1022  
1023  
1024  
1025  
1026  
1027  
1028  
1029  
1030  
1031  
1032  
1033  
1034  
1035  
1036  
1037  
1038  
1039  
1040  
1041  
1042  
1043  
1044  
1045  
1046  
1047  
1048  
1049  
1050  
1051  
1052  
1053  
1054  
1055  
1056  
1057  
1058  
1059  
1060  
1061  
1062  
1063  
1064  
1065  
1066  
1067  
1068  
1069  
1070  
1071  
1072  
1073  
1074  
1075  
1076  
1077  
1078  
1079  
1080  
1081  
1082  
1083  
1084  
1085  
1086  
1087  
1088  
1089  
1090  
1091  
1092  
1093  
1094  
1095  
1096  
1097  
1098  
1099  
1100  
1101  
1102  
1103  
1104  
1105  
1106  
1107  
1108  
1109  
1110  
1111  
1112  
1113  
1114  
1115  
1116  
1117  
1118  
1119  
1120  
1121  
1122  
1123  
1124  
1125  
1126  
1127  
1128  
1129  
1130  
1131  
1132  
1133  
1134  
1135  
1136  
1137  
1138  
1139  
1140  
1141  
1142  
1143  
1144  
1145  
1146  
1147  
1148  
1149  
1150  
1151  
1152  
1153  
1154  
1155  
1156  
1157  
1158  
1159  
1160  
1161  
1162  
1163  
1164  
1165  
1166  
1167  
1168  
1169  
1170  
1171  
1172  
1173  
1174  
1175  
1176  
1177  
1178  
1179  
1180  
1181  
1182  
1183  
1184  
1185  
1186  
1187  
1188  
1189  
1190  
1191  
1192  
1193  
1194  
1195  
1196  
1197  
1198  
1199  
1200  
1201  
1202  
1203  
1204  
1205  
1206  
1207  
1208  
1209  
1210  
1211  
1212  
1213  
1214  
1215  
1216  
1217  
1218  
1219  
1220  
1221  
1222  
1223  
1224  
1225  
1226  
1227  
1228  
1229  
1230  
1231  
1232  
1233  
1234  
1235  
1236  
1237  
1238  
1239  
1240  
1241  
1242  
1243  
1244  
1245  
1246  
1247  
1248  
1249  
1250  
1251  
1252  
1253  
1254  
1255  
1256  
1257  
1258  
1259  
1260  
1261  
1262  
1263  
1264  
1265  
1266  
1267  
1268  
1269  
1270  
1271  
1272  
1273  
1274  
1275  
1276  
1277  
1278  
1279  
1280  
1281  
1282  
1283  
1284  
1285  
1286  
1287  
1288  
1289  
1290  
1291  
1292  
1293  
1294  
1295  
1296  
1297  
1298  
1299  
1300  
1301  
1302  
1303  
1304  
1305  
1306  
1307  
1308  
1309  
1310  
1311  
1312  
1313  
1314  
1315  
1316  
1317  
1318  
1319  
1320  
1321  
1322  
1323  
1324  
1325  
1326  
1327  
1328  
1329  
1330  
1331  
1332  
1333  
1334  
1335  
1336  
1337  
1338  
1339  
1340  
1341  
1342  
1343  
1344  
1345  
1346  
1347  
1348  
1349  
1350  
1351  
1352  
1353  
1354  
1355  
1356  
1357  
1358  
1359  
1360  
1361  
1362  
1363  
1364  
1365  
1366  
1367  
1368  
1369  
1370  
1371  
1372  
1373  
1374  
1375  
1376  
1377  
1378  
1379  
1380  
1381  
1382  
1383  
1384  
1385  
1386  
1387  
1388  
1389  
1390  
1391  
1392  
1393  
1394  
1395  
1396  
1397  
1398  
1399  
1400  
1401  
1402  
1403  
1404  
1405  
1406  
1407  
1408  
1409  
1410  
1411  
1412  
1413  
1414  
1415  
1416  
1417  
1418  
1419  
1420  
1421  
1422  
1423  
1424  
1425  
1426  
1427  
1428  
1429  
1430  
1431  
1432  
1433  
1434  
1435  
1436  
1437  
1438  
1439  
1440  
1441  
1442  
1443  
1444  
1445  
1446  
1447  
1448  
1449  
1450  
1451  
1452  
1453  
1454  
1455  
1456  
1457  
1458  
1459  
1460  
1461  
1462  
1463  
1464  
1465  
1466  
1467  
1468  
1469  
1470  
1471  
1472  
1473  
1474  
1475  
1476  
1477  
1478  
1479  
1480  
1481  
1482  
1483  
1484  
1485  
1486  
1487  
1488  
1489  
1490  
1491  
1492  
1493  
1494  
1495  
1496  
1497  
1498  
1499  
1500  
1501  
1502  
1503  
1504  
1505  
1506  
1507  
1508  
1509  
1510  
1511  
1512  
1513  
1514  
1515  
1516  
1517  
1518  
1519  
1520  
1521  
1522  
1523  
1524  
1525  
1526  
1527  
1528  
1529  
1530  
1531  
1532  
1533  
1534  
1535  
1536  
1537  
1538  
1539  
1540  
1541  
1542  
1543  
1544  
1545  
1546  
1547  
1548  
1549  
1550  
1551  
1552  
1553  
1554  
1555  
1556  
1557  
1558  
1559  
1560  
1561  
1562  
1563  
1564  
1565  
1566  
1567  
1568  
1569  
1570  
1571  
1572  
1573  
1574  
1575  
1576  
1577  
1578  
1579  
1580  
1581  
1582  
1583  
1584  
1585  
1586  
1587  
1588  
1589  
1590  
1591  
1592  
1593  
1594  
1595  
1596  
1597  
1598  
1599  
1600  
1601  
1602  
1603  
1604  
1605  
1606  
1607  
1608  
1609  
1610  
1611  
1612  
1613  
1614  
1615  
1616  
1617  
1618  
1619  
1620  
1621  
1622  
1623  
1624  
1625  
1626  
1627  
1628  
1629  
1630  
1631  
1632  
1633  
1634  
1635  
1636  
1637  
1638  
1639  
1640  
1641  
1642  
1643  
1644  
1645  
1646  
1647  
1648  
1649  
1650  
1651  
1652  
1653  
1654  
1655  
1656  
1657  
1658  
1659  
1660  
1661  
1662  
1663  
1664  
1665  
1666  
1667  
1668  
1669  
1670  
1671  
1672  
1673  
1674  
1675  
1676  
1677  
1678  
1679  
1680  
1681  
1682  
1683  
1684  
1685  
1686  
1687  
1688  
1689  
1690  
1691  
1692  
1693  
1694  
1695  
1696  
1697  
1698  
1699  
1700  
1701  
1702  
1703  
1704  
1705  
1706  
1707  
1708  
1709  
1710  
1711  
1712  
1713  
1714  
1715  
1716  
1717  
1718  
1719  
1720  
1721  
1722  
1723  
1724  
1725  
1726  
1727  
1728  
1729  
1730  
1731  
1732  
1733  
1734  
1735  
1736  
1737  
1738  
1739  
1740  
1741  
1742  
1743  
1744  
1745  
1746  
1747  
1748  
1749  
1750  
1751  
1752  
1753  
1754  
1755  
1756  
1757  
1758  
1759  
1760  
1761  
1762  
1763  
1764  
1765  
1766  
1767  
1768  
1769  
1770  
1771  
1772  
1773  
1774  
1775  
1776  
1777  
1778  
1779  
1780  
1781  
1782  
1783  
1784  
1785  
1786  
1787  
1788  
1789  
1790  
1791  
1792  
1793  
1794  
1795  
1796  
1797  
1798  
1799  
1800  
1801  
1802  
1803  
1804  
1805  
1806  
1807  
1808  
1809  
1810  
1811  
1812  
1813  
1814  
1815  
1816  
1817  
1818  
1819  
1820  
1821  
1822  
1823  
1824  
1825  
1826  
1827  
1828  
1829  
1830  
1831  
1832  
1833  
1834  
1835  
1836  
1837  
1838  
1839  
1840  
1841  
1842  
1843  
1844  
1845  
1846  
1847  
1848  
1849  
1850  
1851  
1852  
1853  
1854  
1855  
1856  
1857  
1858  
1859  
1860  
1861  
1862  
1863  
1864  
1865  
1866  
1867  
1868  
1869  
1870  
1871  
1872  
1873  
1874  
1875  
1876  
1877  
1878  
1879  
1880  
1881  
1882  
1883  
1884  
1885  
1886  
1887  
1888  
1889  
1890  
1891  
1892  
1893  
1894  
1895  
1896  
1897  
1898  
1899  
1900  
1901  
1902  
1903  
1904  
1905  
1906  
1907  
1908  
1909  
1910  
1911  
1912  
1913  
1914  
1915  
1916  
1917  
1918  
1919  
1920  
1921  
1922  
1923  
1924  
1925  
1926  
1927  
1928  
1929  
1930  
1931  
1932  
1933  
1934  
1935  
1936  
1937  
1938  
1939  
1940  
1941  
1942  
1943  
1944  
1945  
1946  
1947  
1948  
1949  
1950  
1951  
1952  
1953  
1954  
1955  
1956  
1957  
1958  
1959  
1960  
1961  
1962  
1963  
1964  
1965  
1966  
1967  
1968  
1969  
1970  
1971  
1972  
1973  
1974  
1975  
1976  
1977  
1978  
1979  
1980  
1981  
1982  
1983  
1984  
1985  
1986  
1987  
1988  
1989  
1990  
1991  
1992  
1993  
1994  
1995  
1996  
1997  
1998  
1999  
2000  
2001  
2002  
2003  
2004  
2005  
2006  
2007  
2008  
2009  
2010  
2011  
2012  
2013  
2014  
2015  
2016  
2017  
2018  
2019  
2020  
2021  
2022  
2023  
2024  
2025  
2026  
2027  
2028  
2029  
2030  
2031  
2032  
2033  
2034  
2035  
2036  
2037  
2038  
2039  
2040  
2041  
2042  
2043  
2044  
2045  
2046  
2047  
2048  
2049  
2050  
2051  
2052  
2053  
2054  
2055  
2056  
2057  
2058  
2059  
2060  
2061  
2062  
2063  
2064  
2065  
2066  
2067  
2068  
2069  
2070  
2071  
2072  
2073  
2074  
2075  
2076  
2077  
2078  
2079  
2080  
2081  
2082  
2083  
2084  
2085  
2086  
2087  
2088  
2089  
2090  
2091  
2092  
2093  
2094  
2095  
2096  
2097  
2098  
2099  
2100  
2101  
2102  
2103  
2104  
2105  
2106  
2107  
2108  
2109  
2110  
2111  
2112  
2113  
2114  
2115  
2116  
2117  
2118  
2119  
2120  
2121  
2122  
2123  
2124  
2125  
2126  
2127  
2128  
2129  
2130  
2131  
2132  
2133  
2134  
2135  
2136  
2137  
2138  
2139  
2140  
2141  
2142  
2143  
2144  
2145  
2146  
2147  
2148  
2149  
2150  
2151  
2152  
2153  
2154  
2155  
2156  
2157  
2158  
2159  
2160  
2161  
2162  
2163  
2164  
2165  
2166  
2167  
2168  
2169  
2170  
2171  
2172  
2173  
2174  
2175  
2176  
2177  
2178  
2179  
2180  
2181  
2182  
2183  
2184  
2185  
2186  
2187  
2188  
2189  
2190  
2191  
2192  
2193  
2194  
2195  
2196  
2197  
2198  
2199  
2200  
2201  
2202  
2203  
2204  
2205  
2206  
2207  
2208  
2209  
2210  
2211  
2212  
2213  
2214  
221